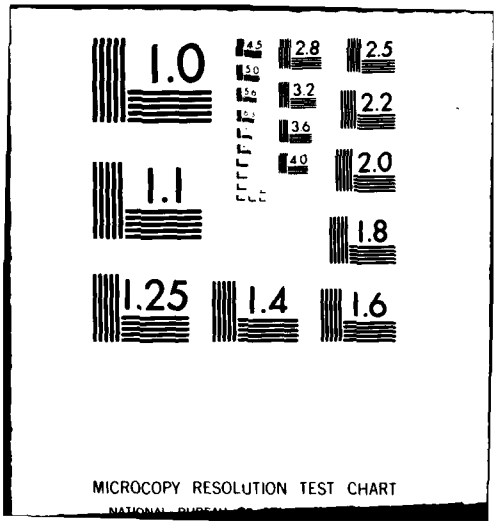
AD-A089 917 OFFICE OF NAVAL RESEARCH LONDON (ENGLAND) F/G 7/4
A REPORT ON THE INTERNATIONAL SYMPOSIUM ON NUCLEAR QUADRUPOLE R--ETC(U)
SEP 80 J C CARTER
UNCLASSIFIED ONRL-C-2-80 NL

END
DATE FILMED
11-80
DTIC


1.0
1.1
1.25
1.4
1.6
1.8
2.0
2.2
2.5
2.8
3.2
3.6
4.0
4.5
5.0
5.6
MICROCOPY RESOLUTION TEST CHART

LEVEL II

10

ONR LONDON CONFERENCE REPORT

C-2-80

OFFICE OF NAVAL RESEARCH

BRANCH OFFICE LONDON ENGLAND

A REPORT ON THE FIFTH INTERNATIONAL SYMPOSIUM ON NUCLEAR QUADRUPOLE RESONANCE SPECTROSCOPY HELD AT THE LABORATOIRE DU COORDINATION DU CNRS TOULOUSE, FRANCE—10-14 SEPT 1979

J. C. Carter*

3 September 1980

*Division of Engineering Research, Louisiana State University

UNITED STATES OF AMERICA

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE	READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER: C-2-80 (de Chimie)	2. GOVT ACCESSION NO.: AD-A089 917	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle): A REPORT ON THE 5th INTERNATIONAL SYMPOSIUM ON NUCLEAR QUADRUPOLE RESONANCE SPECTROSCOPY HELD AT THE LABORATOIRE DU COORDINATION DU CNRS, TOULOUSE, FRANCE 10-14 SEPTEMBER 1979	5. TYPE OF REPORT & PERIOD COVERED (5th)
	PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s): J.C. Carter	8. CONTRACT OR GRANT NUMBER(s): 14
9. PERFORMING ORGANIZATION NAME AND ADDRESS: Office of Naval Research Branch Office London, Box 39, FPO NY 09510	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS: ONRL-C-2-80	12. REPORT DATE: 3 September 1980
	13. NUMBER OF PAGES: 11
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)	15. SECURITY CLASS. (of this report): UNCLASSIFIED
	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

APPROVED FOR PUBLIC RELEASE; DISTRIBUTION UNLIMITED

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Nuclear Quadrupole Resonance Spectroscopy, NQR, Quadrupole Coupling Constant, Asymmetry Parameter, ENDOR, Quadrupole Double Resonance, Computer Data Base of NQR Spectra, NQR Pressure and Temperature Coefficients, Electric Field Gradient (Tenspr), Zeeman Effect, Paramagnetism, Relaxation Times.

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The 5th International Symposium on Nuclear Quadrupole Resonance Spectroscopy took place in Toulouse, France, September 10-14, 1979. Seven invited lectures and a selection from more than 50 contributed papers are reviewed. The variety of topics covered illustrates the extensive potential of NQR spectroscopy in many disciplines of chemistry and physics. Applications ranging from the characterization of bacteriostatic drugs to the remote exploration for minerals are described. The number of papers reporting double resonance

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE

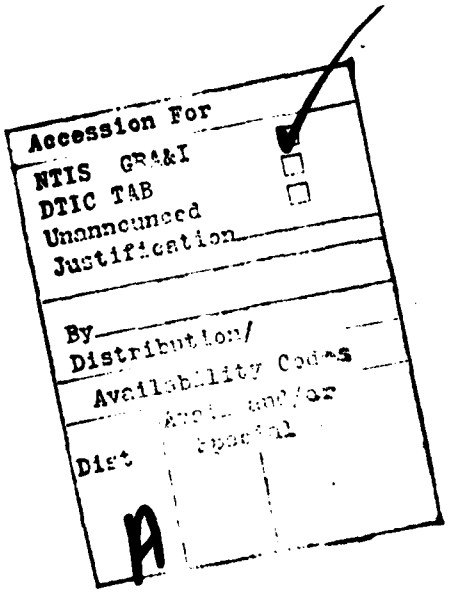
S/N 0102-LF-014-6601

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

265000

investigations, especially those concerned with the biologically important nuclei ^{14}N and ^{17}O, indicates that significant progress is now being achieved in this field.



A REPORT ON THE FIFTH INTERNATIONAL SYMPOSIUM ON NUCLEAR QUADRUPOLE RESONANCE SPECTROSCOPY HELD AT THE LABORATOIRE DE CHIMIE DU COORDINATION DU CNRS TOULOUSE, FRANCE—10-14 SEPTEMBER 1979

Introduction

The origin of the present series of international Nuclear Quadrupole Resonance (NQR) colloquia may be traced to a meeting held in Prof. H. Schimdtbauer's laboratory at the University of Würzburg in April, 1971. Approximately thirty participants from several European countries attended two lectures on NQR spectroscopy. The first, dealing with theoretical and interpretative aspects of the subject was presented by Prof. J.A.S. Smith (Queen Elizabeth College, Univ. of London) while the second, given by Mr. P.M. Butcher (Decca Radar Ltd., London, UK) was concerned with instrumentation. The enthusiasm which was expressed in the questions and informal discussion following these lectures clearly demonstrated that the point had been reached where periodic meetings devoted exclusively to the exchange of information on NQR spectroscopy were urgently needed. Proposals for future meetings were discussed and the idea of the present series was born.

The first of these "International Symposia" was held at Queen Elizabeth College in September, 1972. Smith hosted the meeting which attracted three times as many participants as the Würzburg lectures. Several were from the United States and other non-European countries. The success of the two-day program left no doubt that the initial enthusiasm shown at Würzburg had not waned. An international organizing committee was established and the general format adopted at the London Symposium was retained for subsequent meetings held at Viareggio, Italy in 1973, Tampa, Florida in 1975 and Tokyo, Japan in 1977.

Each meeting was an unqualified success; the scientific programs had to be expanded to cope with the increased numbers of papers submitted and an extremely intense exchange of information and ideas took place. There is no doubt that the relatively small size of the NQR community and the fact that representatives from the majority of laboratories involved in the field worldwide were able to attend contributed greatly to the very special environment which existed at each of those meetings.

The fifth symposium was held at the Coordination Chemistry Laboratory (LCC) of the Centre National de la Recherche Scientifique (CNRS) in Toulouse. Dating back to pre-Roman times, the city has a rich cultural and academic heritage, being the site of one of the first universities in France. Today it is also the center of the French aerospace industry, numerous important chemical and electronic concerns, colleges of advanced technology and several government operated CNRS laboratories.

Formal Opening

Prof. F. Gallais, previous director of the CNRS and LCC acted as chairman for an elaborate opening ceremony. Dr. G. Jugie, co-president of the local organizing committee initiated the proceedings by welcoming the participants. He emphasized the fact that considerable material support had been furnished by the CNRS and that the meeting had received the status of "colloque associé." This official recognition allowed the excellent facilities of the LCC, including a first class lecture theater to be placed completely at the disposal of the symposium participants. Financial support had also been received from the city of Toulouse, the chamber of commerce and the tourist office. In his concluding remarks, Jugie expressed the hope that the fifth symposium would acquire a uniquely French-provincial identity and wished the participants "Bienvenu a Toulouse."

The director of the LCC, Prof. Poilblanc who is responsible for the very close ties which exist between the CNRS and the Université Paul Sabatier, discussed the importance of NQR in the field of coordination chemistry. This application is a speciality of Jugie's group and has proved to be of exceptional value in the investigations of Group III—Group V donor-acceptor complexes conducted at the LCC.

Dr. R. Maurel, scientific director of the CNRS, emphasized the value of specialist international symposia. It is the philosophy of the organization that meetings of this kind are not only beneficial to French science because they greatly facilitate the exchange of ideas and information with experts from other countries but also that they act as a vehicle whereby French achievements are drawn to the attention of the international scientific community. The president of the Université Paul Sabatier, Prof. J.C. Martin, reaffirmed the close links which exist between the university and the CNRS. Prof. H. Chihara, president of the international committee, thanked Jugie and Prof. L. Guibé for their excellent organization of the program commenting that 95% of the task is complete by the time the first participant arrives! Guibé concluded the welcoming remarks but prior to the commencement of the program itself Prof. P. Grivet, the first Frenchman to conduct a NQR experiment, gave a brief historical and scientific introduction.

Scientific Program

This section of the report is confined to reviews of the seven invited lectures and a personal selection of a number of highlights taken from the ten formal sessions where more than 50 other papers were presented.

A significant increase in the number of double resonance experiments has occurred in recent years and the fact that the entire first session of the symposium was devoted to the technique reflected this. Equally noteworthy was the predominance of ^{17}O studies reported at this meeting some of which

were conducted on samples containing the isotope in natural abundance. This biologically important nucleus will undoubtedly be increasingly exploited in the future as techniques are refined.

There are several different kinds of double resonance approach and, to some extent, the experiment must be adapted to suit the molecular architecture of the system under investigation. This lack of generality has probably hindered development in the NQR field in the past but there now exists sufficient readily available literature to minimize this difficulty in the future.

In the first invited paper, Smith reviewed double resonance techniques with emphasis on their suitability for ^{17}O measurements and the influence of various relaxation processes on the quality of the spectra obtained. Data were presented for species containing symmetric and asymmetric hydrogen bonds. In the symmetric class, for example, coupling constants of the order of 6 MHz and asymmetry parameters near 0.6 were found for potassium dihydrogen dibenzoate. These values are quite characteristic of symmetrical O...H...O hydrogen bonds and similar values are found in many other acid salts. Surprisingly large variations in the ^{17}O NQR parameters for closely related compounds in the asymmetric H-bond category were observed even to the extent of reversal of the sign of the coupling constant. Such results may be related to the 2p electron density distribution around the oxygen atom but there is still a serious lack of information concerning the orientation of the electric field gradient tensor with respect to the molecular frame of reference.

A new technique for detecting NQR of rare nuclei called double resonance with coupled multiplets was reported by S.G.P. Brosnan (*Oxford Univ., UK*). Relying on the splitting of nucleus and neighboring protons, the method enables natural abundance spectra to be observed easily with much less applied radio-frequency power than previously possible. Results obtained using this new method show that some previously published data for isotopically enriched samples using double resonance with level crossing have been misinterpreted.

A very interesting lecture was given by O. Lumpkin (Univ. of California, San Diego, CA) concerning aspects of electronic structure revealed by proton double resonance detection of ^{17}O NQR transitions in ozone, hydrogen peroxide, ice and Vask's compound. No sample shifting mechanism was used; instead, the magnetic field applied to the sample was cycled electronically. Peak fields of the order of 0.25T were achieved. Irradiation of the quadrupolar spin system and detection of the proton spin echo signal at 1.8 MHz was accomplished within 50 ms of the application of the polarizing magnetic field. Sample volumes of approximately 0.1 ml were used. The fact that double resonance was observed in ice at 1.5 K without phase modulation was ascribed to proton tunnelling in a symmetric double potential well, and the quadrupole parameters measured for reversibly bound dioxygen in Vaska's compound $\{IrO_2Cl(CO)[P(C_6H_5)_3]_2\}$ were remarkably similar to those of the peroxide ion.

The second session began with an invited paper given by Prof. A. Colligiani (Laboratorio di Chimica Quantistica ed Energetica Molecolare, Pisa, Italy) on the subject of obtaining NQR data from electron-nuclear double resonance (ENDOR) experiments. The technique consists of introducing a radiofrequency field, Hr, suitably oriented with respect to the static field, Ho, inside the microwave cavity of an ESR spectrometer. The unpaired electron energy levels are split into a whole series of sublevels by interaction with the nuclear spins giving rise to a set of allowed transitions at frequencies ranging from a few kilohertz to hundreds of megahertz. A study of the variation of the measured ENDOR frequencies when a single crystal is rotated about three orthogonal axes gives quite precise values of the hyperfine coupling constants even when such interactions are not obtainable from the simple ESR spectrum. The ENDOR measurement is carried out by saturating one of the ESR transitions and sweeping the frequency of the Hr field. When the resonance condition is met, a redistribution of the electron spin populations partially desaturates the ESR transition causing a corresponding variation in the signal amplitude. The complete ENDOR spectrum is built up by successively monitoring all the ESR transitions. If a single crystal is studied, it is possible to determine all the parameters characterizing the electric field gradient tensor such as η and the orientation of the principal axes. Colligiani reported data obtained for a single crystal of potassium hydrogen malonate having a volume of approximately $3mm^3$. The radical, originating from x-ray irradiation of the crystal, was $HOOCDCOO^-$. The deuterium coupling constant was found to be +0.167 MHz, the asymmetry parameter η=0.0617 and the electric field gradient is rotated around the C-D bond by 14° with respect to the hyperfine tensor.

Current interest in the field of NQR is running at a level where more than 200 papers on the topic are published each year and keeping abreast with the recent literature is becoming very time consuming. Therefore, it was with great interest and considerable enthusiasm that the participants welcomed Prof. H. Chihara's (Osaka Univ., Japan) proposal to build a data base of NQR spectra. Assembly of the data base in computer readable form is being carried out under contract with the Science and Technology Agency of the Japanese government. The contents of the data base include: chemical names (systematic, common, trade, etc.), Chemical Abstracts registry number, nuclear species, temperature, resonance frequencies, references and key words. The data may be distributed as a tape file, data book, compilation of bibliography or data cards with one card per substance. Anyone who produces NQR spectral data is invited to assist Chihara by sending him complete information and publication pre-prints.

Interesting applications of short range remote (i.e., external to the instrument) detection of NQR signals were described by T. Hirschfeld (Lawrence Livermore Laboratories, Univ. of California). Using a high power pulsed Fourier Transform spectrometer driving a ribbon pancake search coil 30 cm in diameter, small quantities of ^{14}N containing compounds such as TNT have been detected at distances of up to 1m. Such an instrument has unexplored potential in searching for explosive devices, drugs and minerals.

R.A. Marino (Hunter College of CUNY, NYC) described a method whereby enhanced coupling of the applied radiofrequency field to small samples was achieved with the aid of coils wound on toroidal ferrite forms. Disc shaped specimens were placed in a radial slot cut in the ferrite torus in such a way that the maximum magnetic field was concentrated in the sample volume. This technique was shown to be particularly suitable for low resonance frequencies and moderate temperatures. Unfortunately, since the permeability of the ferrite falls as the temperature is reduced, this approach is unsuitable for measurements at very low temperatures.

Prof. Y. Abe (Univ. of Tsukuba, Japan) discussed the temperature dependence of the ^{14}N NQR resonances in certain hydrazine derivatives on the basis of the Bayer-Kushida theory. All the observed ν^+ lines show normal temperature dependence but several ν_- signals exhibit anomalous behavior. In the case of N, N dimethyl hydrazine, the ν_- signal increases in frequency by 400 Hz as the temperature is raised from 4.2 to 40 K. These results were interpreted on the basis of temperature dependence of the principal components of the electric field gradient tensor arising from changes in the molecular orbital electron populations.

NQR pressure dependence measurements conducted at low temperatures offer a potential tool for the study of molecular interactions in crystals. R.J.C. Brown (Queen's Univ., Kingston, Ontario, Canada) reviewed the theoretical description of this phenomenon due to Kushida, Benedek, and Bloombergen and presented experimental results for a number of molecular crystals such as parachlorophenol and antimony trichloride. The pressure coefficient c contains both static and dynamic terms; increased pressure changes the average intermolecular distances and hence affects the resonance frequencies, the amplitudes of torsional oscillations are also decreased and so the reduction of the quadrupole frequency is made smaller. To some extent these effects can be separated by measurement of the pressure coefficient at several different temperatures. The assumption that the quadrupole resonance frequency is a function of temperature and volume only is, however, too simple; all the parameters which affect the crystal geometry may contribute. Yet for most substances very little is known about the variation of the crystallographic parameters with temperature and pressure. In spite of this, qualitative trends are apparent which suggest the NQR pressure dependence measurements are a good probe for intermolecular forces.

Quadrupole interactions in fluctuating valence rare earth systems were reported by L.C. Gupta (Tata Institute of Fundamental Research, Bombay, India). In compounds of the type R.E. Cu_2Si_2 the average valency of the rare earth and the copper quadrupole coupling constants vary with temperature. Measurements for $EuCu_2Si_2$ over the temperature interval 77-500K show that the quadrupole coupling constant changes from 5.9 to 3.0 MHz and the valency of the europium ion varies from 2.3 to 2.9 in this material.

The problem of anomalous temperature coefficients in pure quadrupole resonance was tackled by Prof. E.A.C. Lucken (Universität de Genève, Switzerland) in the third invited lecture. Lucken suggested that this interesting phenomenon is comparatively rare. In my view this impression results from a scarcity of measurements of central metal resonances where complex electronic and vibrational factors come into play; our current idea of "normality" is distorted by consideration of a sample which is heavily biased in favor of terminal halogen data. The mathematical analysis of the temperature variation of resonance frequencies is severely complicated by solid state effects. It is therefore natural to seek a simple insight into the fundamental processes responsible for the phenomenon by considering isolated molecules in the gas phase. Results of a survey of the vibrational dependence of quadrupole coupling constants derived from microwave spectroscopy and theoretical calculations were presented. It was concluded that for most polyatomic molecules terms are present which give rise to positive temperature coefficients, but in most cases these are swamped by the effect of librational motions.

A very different aspect of this subject was discussed by Prof. N. Nukamura (Osaka Univ., Japan) who reported the anamalous temperature dependence of NQR frequencies in some ammonium salts. Compounds such as α-NH_4HgCl_3 and NH_4ReO_4 show positive or nearly zero temperature coefficients between 100 and 300 K. The correlation times for the reorientation of ammonium ions was found to be about 10^{-12}s at 300 K and the existence of strong electrostatic interactions between the quadrupolar metal nuclei and the NH_4^+ groups has been suggested. Such anomalous behavior may be interpreted by taking into account the finite jump-time of the NH_4^+ ions between possible equivalent equilibrium orientations. If the process occurs with sufficient rapidity, an averaged NQR resonance frequency is observed. In this work NMR results were used to fit experimental NQR data and thus obtain estimates for the magnitude of the jump-time. The effect of selective hydrogen bonding between chlorine and protons of the ammonium group in NH_4HgCl_3 was also discussed.

NQR Zeeman studies and the crystal structure of $CaSnCl_6 \cdot 6H_2O$ were described by M. Suhara (Kanazawa Univ., Japan). The ^{35}Cl NQR temperature dependence of this compound is extremely unusual in that a local minimum frequency of 15.90 MHz at 230 K and a local maximum of 15.92 MHz at 370 K are observed. At room temperature this substance crystallizes in the hexagonal space group $R\bar{3}$ with three molecules per unit cell. The complex ions $Ca(H_2O)_6^{2+}$ and $SnCl_6^{2-}$ form a rhombohedrally distorted CsCl type structure. Three distinct types of hydrogen bond exist in the structure; one parallel to the c-axis, and the others perpendicular to it. The asymmetry parameter is 0.035 and the x and y axes of the EFG tensor are directed along hydrogen bonds between chlorine atoms and water molecules. Proton NMR and ESR line shapes indicated that the anomaly in the NQR data originates in thermal motion associated with the hydrogen bonding. Several successive phase transitions were found by x-ray diffraction, DTA and ESR measurements. A compound which exhibits such a wealth of interesting effects clearly deserves further attention.

The electronic structure of tricarbonyl cyclohexadienyl maganese(I) and its substituted analogues based on ^{55}Mn NQR spectroscopy was discussed by Prof. T.B. Brill (Univ. of Delaware). The ^{55}Mn spectra yield information about the contact between the metal orbitals and the ring carbon atoms. Coupling constants generally are in the range 48-66 MHz and a marked correlation with stereochemistry is observed. The asymmetry parameters are very large (0.5-0.7) and in the case of $C_6H_7Mn(CO)_3$ the forbidden $5/2 \leftrightarrow 1/2$ transition was actually observed. The dependence of transition probability on the magnitude of the asymmetry parameter was treated and the quantitative correctness of Cohen's tables supported. Definite trends were found in both asymmetry parameter and coupling constant when the nature of the substituent X was varied in $C_6H_6XMn(CO)_3$. One of the important features of this paper is that it clearly demonstrates the practicality of ^{55}Mn spectroscopy and it should not only encourage similar investigations but also serve as a stimulus for the exploration of the potential of other transition metals as NQR subjects.

The rapid growth of NQR as a tool for the investigation of phase transitions was reviewed by J.R. Brookeman (Univ. of Florida, Gainsville) in the fourth invited lecture. In NQR, major contributions to the electric field gradient are intramolecular in origin, and so the Hamiltonian is mainly determined by the local static and dynamic environment of the nucleus. In this situation quadrupole resonance spectroscopy can be a very sensitive probe of transition behavior, measuring atomic displacements of less than 0.01 Å and locating transition temperatures with millidegree accuracy. Recent improvements in technique, such as pulse spectrometers with quadrature Fourier Transform capabilities have permitted greater sensitivity and resolution while double resonance procedures have extended the method to other useful but rare species like ^{17}O and ^{2}D. A particular advantage of NQR is the absence of constraints imposed by a large magnet; this facilitates the use of precision cryostats and large pressure bombs and enables phase transitions to be mapped out as functions of temperature and pressure with relative ease. While NQR measurements are most profitably employed in combination with other physical techniques, they make a unique contribution as a microscopic probe of the local properties of phase transitions. Brookeman concluded his lecture by presenting data illustrating the detection of pretransitional clusters which he termed "ferro electric embryos."

NQR spectroscopy also furnishes information concerning changes in electronic charge distributions which occur at metal centers by the action of coordinating ligands. This was the topic of the fifth invited lecture which was given by Prof. T.L. Brown (Univ. of Illinois, Urbana) who stressed that a proper interpretation of NQR data in terms of metal ligand interactions requires careful consideration of the coordination geometry. Metal resonances from isotopes such as ^{59}Co and ^{105}Pd yield information concerning, for example, cis-trans isomerism and the covalency of metal-ligand bonds. However, the

coupling constants and asymmetry parameters are determined by many variables and it is often simpler to observe signals from quadrupolar nuclei contained in the ligands, e.g., ^{35}Cl and ^{14}N. Examples from the coordination complexes of the halogens included data for the MCl_6^{2-} ion in which the trend of resonance frequencies for M+W to Pt cannot be explained merely by invoking differences in the metal electronegativities. The application of double resonance techniques has increased the ability to observe ^{14}N spectra of coordinated nitrogen. A "coordinated nitrogen" model based on the Townes Dailey theory permits a simple yet effective interpretation of the data in terms of the extent of charge transfer from nitrogen to the metal or other Lewis acid center. Extensive results for thiocyanate, pyridine imidazole phenanthroline and glycine complexes of a number of transition metals were used to illustrate the method, and the feasibility of its extension to metal-enzyme systems was discussed.

Metal and halogen NQR data for the quasi-one-dimensional compounds $CuBr_2$, $CuCl_2$, $CsCuBr_3$ and $RbCuCl_3$ was reported by T. Bastow (CSIRO, Victoria, Australia). The Cu resonance in $CuBr_2$ disappeared sharply at 82K although the Br resonance could still be measured by 77K indicating a phase change to an antiferromagnetic state. The observation of metal resonances in these S=1/2 compounds may be due to an exchange narrowing process which is facilitated by the one-dimensional halogen bridged structure. Other compounds of the form $MCuCl_3$ and M_2CuCl_4 characterized by discrete $CuCl_4^{2-}$ and $Cu_2Cl_6^{2-}$ groups were examined unsuccessfully.

In a most impressive discussion concerning NQR studies of biological activity, P.J. Bray (Brown Univ., RI) demonstrated the progress which has been made in this field. NQR-derived molecular charge densities can now be used to understand the biological activity of various compounds. Nitrogen-14 data have been used to establish a linear correlation between the (σNH-σNS) electron densities at the sulphamyl nitrogen of benzene sulphonamides and the *in vitro* carbonic anhydrase inhibitary activities of these sulphonamides. There is a significant correlation between the quadrupole coupling constant, derived from solid state measurements, for the primary amino nitrogen of sulphanilamides and the *in vitro* bacteriostatic activity of these drugs. Data for the aniline precursors of these drugs was also presented. The charge difference σNC-π at the pyridimic nitrogens of nicotinic acid derivatives correlate with the ability to inhibit acetylchloline esterase. The trend of correlation suggests that the pyridimic nitrogen rather than the carbonyl group plays a major role in increasing the inhibition potency. Initial data for nitrogen mustards indicates a correlation of the ^{35}Cl NQR frequencies and the ability of these compounds to inhibit two tumor systems in mice. Bray warned that solid state or solubility effects can mask any correlation in certain instances. Nevertheless, the results which he presented leave a lasting impression of the value and future application of this type of work.

A more complete treatment of the theory of NQR based on the approach of considering the lattice as a classical system with random parameters was described by Prof. I.G. Shaposhnikov (Univ. of Perm, USSR) in the sixth invited lecture. In the procedure the lattice parameters and spin system wave function contain random components which are described statisically by means of a distribution function. The scheme has been applied to the Bayer problem of nuclear quadrupole relaxation and offers a more general solution over a wider temperature range than conventional methods.

The final invited lecture was given by Prof. M.A. Whitehead (McGill Univ., Montreal) who discussed the field gradient from the point of view of the theoretical chemist. NQR results provide one of the most sensitive and exacting tests for the quality of wave functions; it is therefore both natural and desirable for exchanges to take place between theoretician and experimentalist. Unfortunately, the constraints imposed on systems which can be adequately studied by theoretical chemists limit the number of substances for which direct comparisons can be made. Solid state effects especially introduce discrepancies between experimental and theoretically obtained values. Whitehead discussed the relationship between the field gradient and other one electron properties in a constrained variational t treatment of minimum basis set wave functions for small molecules such as CO, N_2, LiH and HCl.

A reinvestigation of quadrupole resonance in a number of solids with the object of seeking evidence for hexadecapole interactions was described by S.L. Segel (Queen's Univ. Kingston, Ontario, Canada). The internal consistency of the data for ^{93}Nb, ^{121}Sb, ^{123}Sb, ^{185}Re, ^{187}Re, and ^{209}Bi in a total of eight different compounds was such that it must be concluded that no measurable hexadecapole interactions exist in the materials studied.

In a most impressive lecture, A.L. Porte (Univ. of Glasgow, Scotland) described bromine-81 studies of bromocyclophosphazatrienes. Zeeman studies enabled asymmetry parameters and coupling constants to be separated in the parent compound $N_3P_3Br_6$. The spectra can be used to provide information concerning the P-Br bond length and inductive effects of various substituents. This permits functional groups to be identified and different structural isomers discriminated.

The discussion concerning the assignment of particular resonances to specific stereochemical environments was both lucid and elegant.

Business Meeting

Traditionally, the next venue is selected democratically by the participants from a number of proposed sites offered by delegates wishing to act as host. This time the voting was in favor of Moscow for the 1981 meeting.

The contribution to the field of NQR made by Russian scientists is beyond question but in the light of the political situation which developed soon after this colloquium, the selection is a singularly unfortunate one and it is unlikely that the next symposium will enjoy the unrestricted support shown for the Toulouse meeting.

On an equally somber note the participants learned of the ill health of Prof. T.A. Scott who contributed many pioneer developments in the field of NQR and served as president of the International NQR committee since 1975 where he did much to promote the success of the international symposia. Every delegate present at the meeting signed a letter wishing him a speedy recovery but unfortunately he died from a brain tumor on 29 October 1979 at the age of 49. Tom Scott was a brilliant scientist who will be sadly missed by the NQR community.

Social Program

The symposium participants were presented to the mayor of Toulouse in the Hall des Illustres of the Capitole. A coach tour was organized to the magnificently preserved medieval fortified town of Carcassonne which is situated some 80 km southwest of Toulouse. On the journey the participants were invited to a wine "degustation" and the symposium dinner was held before returning to Toulouse. Interested participants were also permitted to visit the Aerospatiale factory to see the A300 Airbus assembly line and Concorde.

Concluding Remarks

My impression of the 5th International NQR Symposium is that four major advances were made. First, the explosion of double resonance data particularly for rare nuclei. The time has arrived when theories are implemented in practice and sufficient laboratories now possess working spectrometers for the recent stream of results to become a torrent. Second, the widespread vigor with which the problems of mathematical description of quadrupole resonance phenomena, especially anomalous temperature coefficients, were tackled indicates an important change in direction. In the past attempts were, at best, directed towards particular explanations for individual compounds. Now a concerted effort appears to be under way to find a completely satisfactory general solution. Third, the obvious expansion of NQR as a technological tool. Thermometric and pressure measurement applications have been known for many years but current investigations range from the geosciences to medicine. Fourth, the contribution of Prof. Chihara's data base cannot be overestimated since in the future problems of information selection will become increasingly severe.

The 5th Symposium was an unqualified success both from the scientific and social points of view. I would like to conclude this report by acknowledging the excellent preparations made by Dr. Gerard Jugie (Laboratoire de Chimie de Coordination du CNRS associé à l'Université Paul Sabatier, Toulouse). The major burden fell on his shoulders and he met the challenge by organizing a really first class meeting. The great majority of papers esented at the meeting have now been published as the proceedings of the symposium in a special issue of the *Journal of Molecular Structure*, Volume 58, January, 1980.